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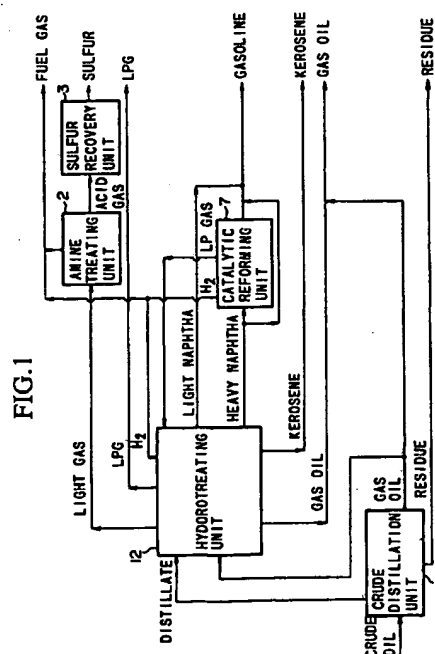
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- (71) Applicant : JGC CORPORATION  
2-1, Otemachi 2-chome  
Chiyoda-ku  
Tokyo (JP)
- (72) Inventor : Kondo, Sadao, c/o Yokohama Office,  
JGC Corp.  
14-1, Bessho 1-chome,  
Minami-ku  
Yokohama-shi, Kanagawa-ken (JP)

**Inventor : Tashiro, Natsuo, c/o Yokohama  
Office, JGC Corp.  
14-1, Bessho 1-chome,  
Minami-ku  
Yokohama-shi, Kanagawa-ken (JP)**  
**Inventor : Ogawa, Akinori, c/o Yokohama  
Office, JGC Corp.  
14-1, Bessho 1-chome,  
Minami-ku  
Yokohama-shi, Kanagawa-ken (JP)**  
**Inventor : Tsuchiya, Fujio, c/o Yokohama  
Office, JGC Corp.  
14-1, Bessho 1-chome,  
Minami-ku  
Yokohama-shi, Kanagawa-ken (JP)**  
**Inventor : Inomata, Makoto, c/o Yokohama  
Office, JGC Corp.  
14-1, Bessho 1-chome,  
Minami-ku  
Yokohama-shi, Kanagawa-ken (JP)**

- 74** Representative : Polus, Camille et al  
c/o Cabinet Lavoix  
2, Place d'Estienne d'Orves  
F-75441 Paris Cedex 09 (FR)

- (54) Refining method and its configuration.**

- (57) The present invention relates to a refinery for hydrotreating of petroleum fractions, and more particularly, a refining method and a refinery configuration comprising a step for distillation of a crude oil to separate a residue and a distillate and a step for hydrotreating the distillate at once in a single hydrotreating unit. If compared to the conventional wherein crude oil is distilled into several fractions and hydrotreating is carried out on each fraction independently, the present invention can simplify a refinery configuration and achieves compact plant with low capital investment cost, even for a small scale refinery.



## Background of the Invention

## Field of the Invention

5 The present invention relates to a refining method and a refinery configuration for separating fractions of gas oil, kerosene, heavy naphtha, light naphtha, LPG, and light gas from crude oil, and for hydrotreating there-  
of.

## Background Art

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Fig. 8 illustrates a conventional refining procedure. Crude oil is supplied to an atmospheric distillation unit 1 pre-treatment such as dehydration and desalting. In the atmospheric distillation unit 1, crude oil is distilled into fractions of light gas, LPG (liquefied petroleum gas), light naphtha, heavy naphtha, kerosene, gas oil, and residue. The light gas (off gas) from the atmospheric distillation unit is amine treated in an amine treating unit 2 together with off gases from other process units to remove an acid gas contained in the off gas. Treated gas is used as a refining fuel gas. The acid gas is sent to a sulfur recovery unit 3 for recovery of sulfur. The LPG fraction is processed in an LPG treating unit 4 for eliminating impurities and is made into an LPG product. The light naphtha fraction is sweetened in a light naphtha treating unit 5 and blended into a high octane reformat. The heavy naphtha fraction is sent to a heavy naphtha hydrotreating unit 6 so as to be hydrotreated in the presence of a catalyst and then sent to a catalytic reforming unit 7 so as to be subjected to isomerization and aromatization and made into high octane reformat for high octane reformat blending. The kerosene fraction is sent to a kerosene treating unit 8 to remove mercaptan sulfur contained in kerosene. The gas oil fraction is sent to a gas oil hydrotreating unit 9 to be hydrotreated in the presence of a catalyst and, after removing impurities, made into a gas oil product. Cracked naphtha (wild naphtha) produced in this process is sent back to the atmospheric distillation unit 1. Residue from the atmospheric distillation unit 1 is used as a blending component of a heavy fuel oil or is further processed in a vacuum distillation unit to obtain a vacuum gas oil.

According to the prior art, regardless of refinery capacity, crude oil is separated into several fractions in distillation unit and then each fraction is hydrotreated or treated independently.

Therefore, a conventional refinery provides a rather complicated configuration and requires large capital investment cost.

Especially for a small scale refinery, development of a compact plant with low capital investment cost has been desired.

## Summary of the Invention

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The present invention has been developed against the above background. An object of the present invention is to provide a novel refining method and refinery configuration in which the refinery is simplified and achieves compact plot plan and low capital investment cost, and which can also be applied to a small scale refinery.

According to the refining method of the present invention, a crude oil is separated into a residue and a distillate which is subjected to hydrotreating all at once in a single hydrotreating unit.

The product obtained by the hydrotreating may be distilled into fractions of gas oil, kerosene, heavy naphtha, light naphtha, LPG, and light gas. Preferably, the separated heavy naphtha is supplied to a catalytic reforming unit where it is converted into a high octane reformat, and at the same time, a hydrogen gas having a purity of 75% or more is recovered from the catalytic reforming unit and supplied to the hydrotreating unit as a make-up hydrogen.

It is also possible to supply an atmospheric residue to a vacuum distillation unit so as to be distilled to obtain a vacuum gas oil and to carry out hydrotreating on the vacuum gas oil together with an atmospheric distillate in a single hydrotreating unit.

As the hydrotreating unit of this refining method, it is preferable to select one of a vapor/liquid co-current down-flow type reactor, a vapor/liquid counter-current type reactor, and a vapor/liquid co-current up-flow type reactor. More preferably, the hydrotreating unit is a vapor/liquid co-current down-flow type reactor or a vapor/liquid co-current up-flow type reactor provided with means for carrying out vapor/liquid separation in the intermediate stage of the reactor.

Furthermore, in this refining method, a part of a product oil obtained by the hydrotreating may be returned to a reactor inlet of the hydrotreating unit.

Preferable hydrotreating conditions are as follows. The pressure is in the range of 20 to 80 kg/cm<sup>2</sup>G, more preferably, 30 to 70 kg/cm<sup>2</sup>G. The temperature is in the range of 300 to 400°C, more preferably, 320 to 380°C. The ratio of hydrogen to oil is in the range of 50 to 200 N1/1, more preferably, 70 to 150 N1/1. The LHSV is in

the range of 0.1 to 5 hr<sup>-1</sup>, more preferably, 1 to 4 hr<sup>-1</sup>.

The refinery configuration according to the present invention comprises an atmospheric distillation unit for distilling a crude oil into a residue and distillate, and a hydrotreating unit for hydrotreating the distillate from the atmospheric distillation unit.

The refinery configuration according to the present invention may comprise a fractionation section for distillation of a product obtained by the hydrotreating in the hydrotreating unit into fractions of gas oil, kerosene, heavy naphtha, light naphtha, LPG, and light gas. The refinery configuration according to the present invention may also comprise a catalytic reforming unit for converting the heavy naphtha fraction into a high octane reformat, and a byproduct hydrogen gas supply line for supplying hydrogen gas recovered from the catalytic reforming unit, to the hydrotreating unit. Furthermore, the refinery configuration according to the present invention may comprise a vacuum distillation unit for distilling an atmospheric residue to obtain a vacuum gas oil and a vacuum gas oil supply line for supplying the vacuum gas oil to the hydrotreating unit for hydrotreating an atmospheric distillate.

In the refinery configuration according to the present invention, it is preferable that the hydrotreating unit is selected from one of a vapor/liquid co-current up-flow type reactor, a vapor/liquid counter-current type reactor, and a vapor/liquid co-current down-flow type reactor. The vapor/liquid co-current down-flow type reactor and the vapor/liquid co-current up-flow type reactor are preferably provided with a vapor/liquid separator in an intermediate stage of the reactor.

Furthermore, the refinery configuration may comprise a product oil return line for returning a part of the product oil obtained in the hydrotreating unit, back to the inlet of the hydrotreating unit.

The refinery configuration according to the present invention has the following advantages.

According to the refinery configuration, a crude oil is distilled under atmospheric pressure into a residue and distillate, and the distillate is hydrotreated all at once in a single hydrotreating unit. The present invention can simplify the refinery configuration to a great degree, and achieve compact plan and all capital investment cost when compared to a conventional refinery configuration in which crude oil is distilled into several fractions and each fraction is hydrotreated independently.

The conventional process in which hydrotreating is carried out for each fraction independently requires maintenance such as catalyst replacement for each hydrotreating unit independently and, accordingly, requires various additional facilities for maintenance. On the other hand, in the refinery configuration according to the present invention in which a distillate is hydrotreated at once in a single hydrotreating unit, maintenance can also be carried out at one time and additional facility for maintenance is significantly simplified. This also reduces the maintenance work and enables effective operation of a refinery.

Besides an atmospheric distillation unit for distillation of a crude oil into a residue and a distillate and a hydrotreating unit for overall hydrotreating of the distillate, the refinery configuration according to the present invention may comprise a fractionation section for separating a product obtained in the hydrotreating unit into fractions of gas oil, kerosene, heavy naphtha, light naphtha, LPG, and light gas, a catalytic reforming unit for converting the heavy naphtha fraction into high octane reformat, and a byproduct hydrogen gas supply line for supplying hydrogen gas recovered from the catalytic reforming unit to the hydrotreating unit. Thus, it is possible to produce the above-mentioned fractions and a major gasoline component and to utilize the byproduct hydrogen gas in the hydrotreating unit as a make-up hydrogen.

Furthermore, the refinery configuration according to the present invention may comprise a vacuum distillation unit for distillation of an atmospheric residue to obtain a vacuum gas oil and a vacuum gas oil supply line for supplying the vacuum gas oil to a hydrotreating unit for hydrotreating an atmospheric distillate. Thus, the feed stock of the hydrotreating unit is increased. That is, the quantity of value-added distillate products is increased.

In the case where a vapor/liquid counter-current type reactor is used as a hydrotreating unit, a distillate is supplied to the intermediate stage between an upper catalyst bed and a lower catalyst bed, where the distillate is separated into a vapor phase (lower boiling point fraction) and a liquid phase (higher boiling point fraction). The higher boiling point fraction containing a large amount of sulfur compounds which is difficult to hydrodesulfurize flows downward so as to contact with hydrogen counter-currently. On the other hand, the lower boiling point fraction which is relatively easy to hydrogenate flows upward co-currently with hydrogen. Thus, it is possible to hydrogenate the total distillate containing several fractions having different boiling points and various types of sulfur compounds which have different reactivities for desulfurization, with high efficiency.

In the case where a hydrotreating unit is a vapor/liquid co-current down-flow type reactor or a vapor/liquid co-current up-flow type reactor having a vapor/liquid separator for vapor/liquid separation in the intermediate stage of the reactor, the distillate is drawn off from the intermediate stage of the reactor so as to separate it into a vapor phase and a liquid phase. One of the vapor phase and the liquid phase can be supplied again to the reactor for further treatment. Thus, it is possible to effectively hydrogenate the distillate containing several

fractions having different boiling points and various sulfur compounds having different reactivities for the sulfurization and to flexibly meet various product specifications for each fraction.

Furthermore, the refinery configuration according to the present invention may also comprise a product oil return line for returning a part of the product oil obtained by hydrotreating, to the reactor inlet of the hydrotreating unit. Thus, it is possible to repeat the hydrotreating on a particular fraction, and the particular fraction can easily be further hydrotreated, if required.

#### Brief Description of the Drawings

Fig. 1 is a flowdiagram illustrative of an example of the refinery configuration according to the present invention.

Fig. 2 illustrates a first example of the preferable hydrotreating unit in the refinery configuration according to the present invention.

Fig. 3 illustrates a second example of the preferable hydrotreating unit in the refinery configuration according to the present invention.

Fig. 4 illustrates a third example of the preferable hydrotreating unit in the refinery configuration according to the present invention.

Fig. 5 illustrates a fourth example of the preferable hydrotreating unit in the refinery configuration according to the present invention.

Fig. 6 illustrates a fifth example of the preferable hydrotreating unit in the refinery configuration according to the present invention.

Fig. 7 illustrates a sixth example of the preferable hydrotreating unit in the refinery configuration according to the present invention.

Fig. 8 is a flowdiagram illustrative of the conventional refinery configuration.

#### Detailed Description of the Preferred Embodiments

Fig. 1 illustrates a refining method according to the present invention. According to this refining method, a crude oil which has been subjected to pre-treatment such as dehydration and desalting is supplied to a crude distillation unit (an atmospheric distillation unit) 11 where a crude oil is distilled at atmospheric pressure into a distillate containing gas oil, kerosene, naphtha, LPG, and light gas and a residue.

The distillate from the crude distillation unit 11 is supplied all together to a hydrotreating unit 12 where it contacts with hydrogen in the presence of a catalyst so as to be hydrotreated and a product obtained by the hydrotreating is distilled into fractions of a gas oil, a kerosene, a heavy naphtha, a light naphtha, a LPG, and light gas (off gas).

Preferably, the hydrotreating unit 12 is selected from a vapor/liquid co-current down-flow type reactor, a vapor/liquid counter-current type reactor, a vapor/liquid co-current up-flow type reactor, and a reactor provided with vapor/liquid separator in the reactor intermediate stage. Hydrogen ( $H_2$ ) gas used in the hydrotreating unit may be a hydrogen gas which is recovered from a catalytic reforming unit 7 where the hydrotreated heavy naphtha is converted into a high octane reformat. The recovered hydrogen gas preferably has a purity of 75% or more, and more preferably 80% or more.

According to the present invention, a crude oil is distilled under atmospheric pressure to separate into a residue and a distillate and the distillate is hydrotreated all at once in a single hydrotreating unit. When compared to the conventional refinery configuration in which a crude oil is separated into several fractions and then each fraction is hydrotreated or treated independently, the refining method according to the present invention can simplify a refining configuration as well as achieves a compact plant and low capital investment cost, even for a small scale refinery.

According to the present invention, a crude oil is distilled under atmospheric pressure into a residue and a distillate. The distillate may be obtained as one distillate including all the fractions excluding the atmospheric residue (gas oil, kerosene, naphtha, LPG, and light gas) or as several fractions separated. For example, it is possible to obtain a gas oil fraction and a kerosene and light fraction separately in atmospheric distillation.

It is also possible to obtain a fraction which does not require hydrotreating separately from a distillate which require hydrotreating. If light gas does not require hydrotreating, for example, it is possible to separate a distillate into light gas and LPG and heavier gas which is processed in the hydrotreating unit. If a distillate containing light gas is obtained in the atmospheric distillation unit, it is possible to remove the light gas before supplying the distillate to the hydrotreating unit.

According to the present invention, a distillate obtained in a single fraction or a distillate fraction requiring hydrotreating is introduced into a single hydrotreating unit and subjected to hydrotreating all at once. A fraction

not requiring hydrotreating which is obtained in atmospheric distillation can also be supplied to the hydrotreating unit. The hydrotreating is preferably carried out under the following conditions. The pressure is in the range of 20 to 80 kg/cm<sup>2</sup>G, more preferably, 30 to 70 kg/cm<sup>2</sup>G. The temperature is in the range of 300 to 400°C, more preferably, 320 to 380°C. The H<sub>2</sub>/oil ratio is in the range of 50 to 200 N1/1, more preferably, 70 to 150 N1/1. The LHSV is in the range of 0.1 to 5 hr<sup>-1</sup> more preferably, 1 to 4 hr<sup>-1</sup>. The hydrogen source may be any gas containing hydrogen, preferably, having a purity of 60% or above.

Any catalyst capable of hydrotreating can be used as the catalyst for the hydrotreating. For example, Co-Mo, Ni-Mo, Co-Mo-P and W-Ni-Mo are commonly used.

Fig. 2 illustrates a vapor/liquid co-current down-flow type reactor as a first example of the hydrotreating unit. The hydrotreating unit comprises a reactor 21 filled with a hydrogenating catalyst 20, a vapor/liquid separator 25, and a fractionation section 23 as main components. For hydrotreating and fractionation using this unit, a distillate consisting of, for example, a gas oil and a kerosene and lighter fraction is supplied together with hydrogen to an upper portion of the reactor 20 and the vapor/liquid mixture is passed downward and the distillate is hydrotreated at a predetermined temperature and a predetermined pressure. The product is drawn off from a bottom of the reactor 21 and supplied to the vapor/liquid separator 25 where the product is separated into a vapor phase (unreacted hydrogen, cracked gas, and others) and a liquid phase (a product oil). The liquid phase is supplied to the fractionation section 23 while the vapor phase, after removing the cracked gas such as hydrogen sulfide, can be recycled to the reactor 21. The liquid phase supplied to the fractionation section 23 is distilled into fractions of gas oil, kerosene, naphtha, LPG, and light gas. Incidentally, the gas oil fraction may be returned to the reactor 21 so as to be hydrotreated again, if necessary.

Fig. 3 illustrates a second example of the hydrotreating unit which is a vapor/liquid co-current up-flow type reactor having an intermediate vapor/liquid separator. In the same way as the hydrotreating unit illustrated in Fig. 2, a hydrotreating unit of the second example comprises: a reactor 21 in which a hydrogenating catalyst 20 is arranged in a plurality of stages, an intermediate vapor/liquid separator 22, a vapor/liquid separator 25, and a fractionation section. For carrying out hydrotreating on a distillate using this hydrotreating unit, a distillate and hydrogen are supplied to a bottom of the reactor 21 and the distillate and hydrogen flow upward so as to hydrotreat the distillate under a predetermined temperature and a predetermined pressure. An effluent coming out of the lower catalyst bed is supplied to the intermediate vapor/liquid separator 22 where it is separated into a vapor phase and a liquid phase. The vapor phase further goes through the upper catalyst bed and is taken out from the top of the reactor to be cooled down and sent to the vapor/liquid separator 25 to be separated into a off gas and a product oil. The liquid phase coming out of the intermediate vapor/liquid separator 22 and the effluent from the vapor/liquid separator 25 are separately or together sent to the fractionation section where the fractions of gas oil, kerosene, naphtha, LPG, and off gas are separated.

Fig. 4 illustrates a third example of the hydrotreating unit which is a vapor/liquid co-current down-flow type reactor having an intermediate vapor/liquid separator. In the same way as the hydrotreating unit illustrated in Fig. 2, the third example of the hydrotreating unit comprises: a reactor 21 having a hydrogenating catalyst 20 arranged in a plurality of stages, an intermediate vapor/liquid separator 22, a vapor/liquid separator 25, and a fractionation unit.

For carrying out hydrotreating using this unit, a distillate and hydrogen are supplied to an upper portion of the reactor 21 and while they are flowing downward inside the reactor, the distillate is hydrotreated under a predetermined temperature and a predetermined pressure. The vapor/liquid mixture is drawn off from a bottom of the upper catalyst bed and is sent to the intermediate vapor/liquid separator 22 where the mixture is separated into a vapor phase and a liquid phase. The vapor phase coming out of the intermediate vapor/liquid separator 22 is cooled down and sent to the vapor/liquid separator 25 where it is separated into a liquid phase and an off gas. The liquid phase separated in the intermediate vapor/liquid separator 22 is flown downward through the lower catalyst bed together with an additional hydrogen for further hydrotreating. The effluent drawn off from a bottom of the reactor 21 and the effluent drawn off from the vapor/liquid separator 25 are separately or together sent to the fractionation section where they are separated into the fractions of gas oil, kerosene, naphtha, LPG, and others.

Fig. 5 illustrates a fourth example of the hydrotreating unit which is a vapor/liquid counter-current type reactor. The hydrotreating unit of the fourth example comprises a reactor 21 having a hydrogenating catalyst 20 arranged in a plurality of stages, a heat exchanger 24, a vapor/liquid separator 25, a hydrogen sulfide removing unit 26, a recycling compressor 27, and a fractionation unit.

For carrying out hydrotreating using this unit, a distillate is supplied to an intermediate stage between an upper and a lower catalyst beds while hydrogen is supplied from a bottom of the reactor 21. The distillate in the intermediate stage is separated into a vapor phase comprising fraction having lower boiling points and a liquid phase comprising fraction having higher boiling points. The liquid phase flows downward through the lower catalyst bed and hydrotreated by contacting with hydrogen counter-currently. The vapor phase flows up-

ward through the upper catalyst bed co-currently with hydrogen gas. The hydrotreated vapor phase which is taken out of the top of the reactor contains fraction having lower boiling points, unreacted hydrogen, and cracked gas. They are sent to the heat-exchanger 24 so as to be cooled down and then, sent to the vapor/liquid separator 25 to be separated into a liquid phase (fraction having lower boiling points) and a vapor phase. The liquid phase drawn off from the vapor/liquid separator 25 and the effluent drawn off from the bottom of the reactor 21 are separately or together sent to the fractionation section 23 where they are separated into the fractions of gas oil, kerosene, naphtha, LPG, and off gas (light gas). The vapor phase separated in the vapor/liquid separator 25 is sent to the hydrogen sulfide removing unit 26 which is provided with, for example, a pressure swing adsorption (PSA) device. After removing hydrogen sulfide from the vapor phase, the vapor phase is compressed by the recycling compressor 27 and returned to the reactor 21 as a hydrogen recycled gas.

The hydrotreating unit of the fourth example separates a distillate into a vapor phase (fraction having lower boiling points) and a liquid phase (fraction having higher boiling points). The fraction of the higher boiling points containing a large amount of sulfur compounds which are difficult to hydrosulfurize flows down contacting with hydrogen counter-currently so as to be effectively hydrogenated while the fraction of lower boiling points which is relatively easy to hydrogenate flows upward co-currently with hydrogen so as to be hydrogenated. Thus, the hydrotreating unit of this type is capable of effectively hydrogenating the distillate comprising several fractions having different boiling points and different reactivities for desulfurization of sulfur compounds.

Fig. 6 illustrates a hydrotreating unit which is a vapor/liquid co-current down-flow type reactor having intermediate vapor/liquid separator suitable for carrying out further refining of comparatively light fractions. A distillate and hydrogen are supplied to a top of a reactor 21 and subjected to a first treatment in the upper catalyst bed. A fluid coming out of a bottom of the upper catalyst bed is introduced to the intermediate vapor/liquid separator 22 where it is separated into a vapor phase and a liquid phase. The liquid phase is made into a product oil. The vapor phase is supplied to the lower catalyst bed of the reactor 21 for further hydrotreating. A fluid coming out of a bottom of the lower catalyst bed is cooled down and introduced to the vapor/liquid separator 25 where it is separated into a vapor phase and a liquid phase. The vapor phase is used to recover as a fuel or a hydrogen for hydrotreating while the liquid phase is made into a product oil. The liquid phase effluent drawn off from the intermediate vapor/liquid separator 22 and the liquid phase effluent from the vapor/liquid separator 25 are separately or together sent to the fractionation section.

Fig. 7 illustrates a vapor/liquid co-current down-flow type reactor used as a hydrotreating unit capable of effective refining of comparatively light fractions. A distillate is separated into a vapor phase and a liquid phase in a vapor/liquid separator 25A which is provided at an upstream of a reactor 21 having a plurality of catalyst bed 20. The vapor phase is supplied to a top of the reactor while the liquid phase is supplied to an intermediate stage between an upper and a lower catalyst beds. The vapor/liquid mixture coming from a bottom of the reactor is introduced to a first vapor/liquid separator 25B where it is separated into a vapor phase and a liquid phase. A part of the separated vapor phase is returned to the top of the reactor as indicated by a broken line in Fig. 7 while the other part of the vapor phase is cooled down and supplied to a second vapor/liquid separator 25C. The liquid phase from the first vapor/liquid separator 25B is cooled down and sent to the fractionation section together with or separately from the liquid phase from the second vapor/liquid separator which is also sent to the fractionation section. It is also possible to cool down the fluid from the reactor 21 and supply it to a vapor/liquid separator where it is separated into off gas and product oil.

By carrying out the hydrotreating and the fractionation as described above, fractions of gas oil, heavy naphtha, light naphtha, LPG, and off gas can be obtained from the hydrotreating unit 12 illustrated in Fig. 1.

The off gas is supplied to the amine treating unit 2 to produce a fuel gas by removing acid gas. The acid gas is sent to the sulfur recovering unit 3 to recover sulfur.

The LPG is used as an LPG product as it is.

The light naphtha can be directly blended into a high octane reformat or subjected to reforming and sweetening treatments if required.

The heavy naphtha is sent to the catalytic reforming unit 7 where it is subjected to isomerization and aromatization and blended into a high octane reformat. The hydrogen byproduced in the catalytic reforming unit 7 is sent to the hydrotreating unit 12 so as to be used as a hydrogen for hydrogenation while the LPG byproduced can be returned to the hydrotreating unit 12 or mixed with the LPG obtained from the hydrotreating unit 12. The kerosene can be used as a kerosene product as it is. The gas oil can be used as a gas oil product as it is.

The residue from the bottom of the crude distillation unit 11 can be used as a blending component of heavy fuel oil or further processed in a vacuum distillation unit to obtain a vacuum gas oil. At least a part of the vacuum gas oil may be hydrotreated together with an atmosphere distillate from the crude distillation unit 11 in the hydrotreating unit 12.

## Comparative Example: Conventional Refining Method

According to a conventional refinery configuration illustrated in Fig. 8, a crude oil was distilled in an atmospheric distillation unit to separate several fractions, and each fraction was supplied to a hydrotreating unit for hydrotreating. Each fraction has characteristics as described below.

The crude oil used was Arabian light and heavy (50 vol/50 vol) having a specific gravity of 0.8618 and sulfur concentration of 1.818% by weight.

Table 1 shows distillation characteristics and yield for each of the fractions.

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TABLE 1

	True Boiling Point (°C)	Yield (vol %)
LPG	Boiling point of C4 or less	1.05
Light Naphtha	C5 - 82	6.24
Heavy Naphtha	82 - 166	17.17
Kerosene	166 - 232	13.45
Gas Oil	232 - 360	23.04
Atmospheric Residue	360 or above	39.05

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C4: butane

C5: pentane

A hydrotreating reaction test was carried out for each fraction under the following conditions.

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Catalyst: Co-Mo-containing catalyst on market (produced by Syokubai-Kasei Kogyo).

Reactor: Internal diameter 8 mm x length 6000 mm

Amount of the catalyst filled: 96cc

Reactor type: Co-current down-flow type

Hydrogen purity: 70%

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Table 2 shows the conditions of the hydrotreating reaction and the results for each fraction.

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TABLE 2

Reaction Conditions					Results	
Fractions	Pressure kg/cm <sup>2</sup> G	Temperature (°C)	LHSV 1/hr	H <sub>2</sub> /oil ratio	Sulfur content before treatment	Sulfur content after treatment
Light naphtha	10	300	3	0.5*1	100 ppm	> 1 ppm
Heavy naphtha	15	300	2	0.5*1	300 ppm	> 1 ppm
Kerosene	20	300	2	150*2	0.2 wt %	0.002 wt %
Gas oil	50	330	2	200*2	1.4 wt %	0.1 wt %

H<sub>2</sub>/Oil ratio\*1: mol ratioH<sub>2</sub>/Oil ratio\*2: Nm<sup>3</sup>/kiloliter



Example 1: Overall hydrotreating of the sequential fractions from light naphtha through gas oil (1)

The hydrotreating was carried out all at once on the sequential fractions from light naphtha through gas oil (having true boiling points of C5 to 360°C) as raw materials by using the same reactor as in the comparative example 1. The reaction conditions were as follows.

Pressure: 40 kg/cm<sup>2</sup>G  
 Temperature: 330°C  
 H<sub>2</sub>/Oil ratio: 100 Nm<sup>3</sup>/kiloliter  
 LHSV: 3.1 1/hr

Under the above-described conditions, the sequential fractions were hydrotreated all at once and the product after the hydrotreating was distilled into the fractions of light naphtha, heavy naphtha, kerosene, and gas oil. Sulfur content was measured for each product.

The sulfur content was found as follows.

Light naphtha: 0.1 wt ppm  
 Heavy naphtha: 0.3 wt ppm  
 Kerosene: 0.001 wt %  
 Gas oil: 0.20 wt %

The results show that the overall hydrotreating brings about sufficient results compared to the conventional fraction-by-fraction hydrotreating. Judging from the results, it may be said that the present invention can simplify the refinery configuration to a great extent without reducing the hydrotreating effect obtained in the prior art.

Example 2: Overall hydrotreating of the sequential fractions from light naphtha through gas oil (2)

The overall hydrotreating was carried out on the sequential fractions from the light naphtha through the gas oil under the same conditions as in the Example 1 except that the LHSV was 1.2 1/hr and the amount of the catalyst used was 250 cc. The sulfur content was measured for each product.

The results were satisfactory as shown below.

Light naphtha:  $\leq 0.1$  wt ppm  
 Heavy naphtha:  $\leq 0.1$  wt ppm  
 Kerosene: 0.0003 wt %  
 Gas oil: 0.05 wt %

Example 3: Overall hydrotreating by a vapor/liquid counter-current type reactor

The overall hydrotreating was carried out on the same raw materials (the sequential fractions from light naphtha through gas oil) as in Example 1 by using a vapor/liquid counter-current type reactor illustrated in Fig. 5 as the reactor. The catalyst bed in the reactor was divided into two stages: an upper catalyst bed and a lower catalyst bed. The raw materials (the sequential fractions) were supplied to an intermediate stage between the upper catalyst bed and the lower catalyst bed while supplying hydrogen from the bottom of the reactor for the overall hydrotreating under the reaction conditions as follows.

Amount of catalyst in upper bed: 40 cc  
 Amount of catalyst in lower bed: 60 cc  
 Pressure: 40 kg/cm<sup>2</sup>G  
 Temperature: 330°C  
 H<sub>2</sub>/Oil ratio: 100 Nm<sup>3</sup>/kiloliter  
 LHSV: 3.1 1/hr

The product after the hydrotreating was moved to a fractionation section for distillation under atmospheric pressure so as to separate the fractions of light naphtha, heavy naphtha, kerosene, and gas oil. The sulfur content was measured for each product.

The results were as follows.

Light naphtha:  $\leq 0.1$  wt ppm  
 Heavy naphtha:  $\leq 0.1$  wt ppm  
 Kerosene: 0.001 wt %  
 Gas oil: 0.15 wt %

## Example 4: Overall hydrotreating of LPG fraction through gas oil fraction

Treatment was carried out under the same conditions as in Example 1, except for that LPG was additionally used. However, the H<sub>2</sub>/oil ratio and the LHSV were calculated on the basis of feed amounts of light naphtha through gas oil (i.e., excluding the LPG).

The sulfur content for each product was as follows.

Light naphtha:  $\leq 0.1$  wt ppm

Heavy naphtha:  $\leq 0.4$  wt ppm

Kerosene: 0.001 wt %

Gas oil: 0.22 wt %

## Claims

1. A refining method characterised in comprising:
  - (a) separating a crude oil into a residue and a distillate by atmospheric distillation, and
  - (b) hydrotreating the distillate all at once in a single hydrotreating unit.
2. A refining method as claimed in Claim 1, wherein a product obtained by said hydrotreating is distilled into fractions of gas oil, kerosene, heavy naphtha, light naphtha, LPG, and light gas.
3. A refining method as claimed in Claim 2, wherein said heavy naphtha fraction is supplied to a catalytic reforming unit so as to be converted into a high octane reformat, and hydrogen gas having a purity of 75% and above is recorded from the catalytic reforming unit is supplied to said hydrotreating unit.
4. A refining method as claimed in Claim 1, wherein said atmospheric residue is supplied to a vacuum distillation unit so as to be distilled to obtain a vacuum gas oil and the vacuum gas oil is hydrotreated together with said atmospheric distillate in said hydrotreating unit.
5. A refining method as claimed in one of Claim 1 through Claim 4, wherein said hydrotreating unit is selected from one of a vapor/liquid co-current down-flow type reactor, a vapor/liquid counter-current type reactor, and a vapor/liquid co-current up-flow type reactor.
6. A refining method as claimed in Claim 5, wherein each of said vapor-liquid co-current down-flow type reactor and said vapor/liquid co-current up-flow type reactor is provided with vapor/liquid separator for carrying out vapor/liquid separation in an intermediate stage of said reactor.
7. A refining method as claimed in one of Claim 1 through 6, wherein a part of a product obtained by said hydrotreating is returned to a reactor inlet of said hydrotreating unit.
8. A refining method as claimed in one of Claim 1 through Claim 7, wherein conditions of said hydrotreating are defined as follows: pressure in a range from 20 to 80kg/cm<sup>2</sup>G, temperature in a range from 300 to 400°C, H<sub>2</sub>/oil ratio in a range from 50 to 200Nl/l, and LHSV in a range from 0.1 to 5 hr<sup>-1</sup>.
9. A refining method as claimed in one of Claim 1 through 7, wherein conditions of said hydrotreating are defined as follows: pressure in a range from 30 to 70 kg/cm<sup>2</sup>G, temperature in a range from 320 to 380°C, H<sub>2</sub>/oil ratio in a range from 70 to 150Nl/l, and LHSV in a range from 1 to 4 hr<sup>-1</sup>.
10. A refining method as claimed in Claim 1, wherein said distillate and hydrogen are introduced into a top of a vapor/liquid co-current down-flow type reactor filled with a hydrogenating catalyst so as to hydrotreat said distillate, an effluent drawn off from a bottom of said reactor is introduced into a vapor/liquid separator so as to be separated into a vapor phase and a liquid phase, and said vapor phase is circulated to said reactor while said liquid phase is distilled to obtain a product oil, a part of which is recycled to the reactor.
11. A refining method as claimed in Claim 1, wherein said hydrotreating unit is a vapor/liquid co-current down-flow type reactor whose hydrogenating catalyst bed is divided into at least two stages of an upper catalyst bed and a lower catalyst bed, said distillate is supplied together with hydrogen into a top of said reactor so as to hydrotreat said distillate, and an effluent is drawn off from a bottom of said upper catalyst bed to

be sent to a vapor/liquid separator where the effluent separated into a vapor phase and a liquid phase, and either phase is further hydrotreated by passing through said lower catalyst bed.

- 5 12. A refining method as claimed in Claim 1, wherein said hydrotreating unit is a vapor/liquid co-current up-flow type reactor whose hydrogenating catalyst bed is divided into at least two stages of an upper catalyst bed and a lower catalyst bed, said distillate is supplied together with hydrogen to a bottom of said reactor so as to hydrotreat on said distillate, an effluent is drawn off from a top of said lower catalyst bed to be sent to a vapor/liquid separator where the effluent separated into a liquid phase and a vapor phase, and the vapor phase is supplied to a bottom of said upper catalyst bed so as to be further hydrotreated.
- 10 13. A refining method as claimed in Claim 1, wherein said hydrotreating unit is a vapor/liquid counter-current type reactor whose hydrogenating catalyst bed is divided into at least two stages of an upper catalyst bed and a lower catalyst bed, said distillate is supplied to an intermediate stage between said upper catalyst bed and said lower catalyst bed to be hydrotreated by hydrogen supplied from a bottom of said reactor so as to obtain a vapor phase effluent from the top of said reactor and a liquid phase effluent from the bottom of said reactor.
- 15 14. A refining method as claimed in Claim 1, wherein said hydrotreating unit is a vapor/liquid co-current down-flow type reactor whose hydrogenating catalyst bed is divided into at least two stages of an upper catalyst bed and a lower catalyst bed, said distillate is supplied together with hydrogen to a vapor/liquid separator so as to separate a vapor phase and a liquid phase, said vapor phase is supplied to a top of said reactor while said liquid phase is introduced into an intermediate stage between said upper catalyst bed and said lower catalyst bed for hydrotreating and an effluent is drawn off from a bottom of said reactor.
- 20 15. A refinery configuration characterised in comprising:
  - 25 a atmospheric distillation unit for distilling a crude oil into a residue and a distillate; and
  - a hydrotreating unit for hydrotreating at once said distillate separated in said atmospheric distillation unit.
- 30 16. A refinery configuration as claimed in Claim 15, wherein a fractionation section is provided for distilling a product obtained by said hydrotreating in said hydrotreating unit to fractions of gas oil, kerosene, heavy naphtha, light naphtha, LPG, and light gas.
- 35 17. A refinery configuration as claimed in 16, wherein said configuration further comprises a catalytic reforming unit for converting said heavy naphtha fraction into a high octane reformat and a byproduced hydrogen gas supply line for supplying hydrogen gas recovered from said catalytic reforming unit to said hydrotreating unit.
- 40 18. A refinery configuration as claimed in Claim 15, wherein said configuration further comprises a vacuum distillation unit for distilling an atmospheric residue to obtain vacuum gas oil and a vacuum gas oil supply line for supplying said vacuum gas oil to said hydrotreating unit.
- 45 19. A refinery configuration as claimed in one of Claim 15 18, wherein said hydrotreating unit is selected from one of a vapor/liquid co-current down-flow type reactor, a vapor/liquid counter-current type reactor, and a vapor/liquid co-current up-flow type reactor.
- 50 20. A refinery configuration as claimed in Claim 19, wherein either of said vapor/liquid co-current down-flow type reactor and said vapor/liquid co-current up-flow type reactor is provided with vapor/liquid separator for vapor/liquid separation in an intermediate stage of said reactor.
- 55 21. A refinery configuration as claimed in one of Claim 15 through 20, wherein said configuration further comprises a product oil return line for recycling a part of a product oil obtained in said hydrotreating unit to a reactor inlet of said hydrotreating unit.

FIG.1

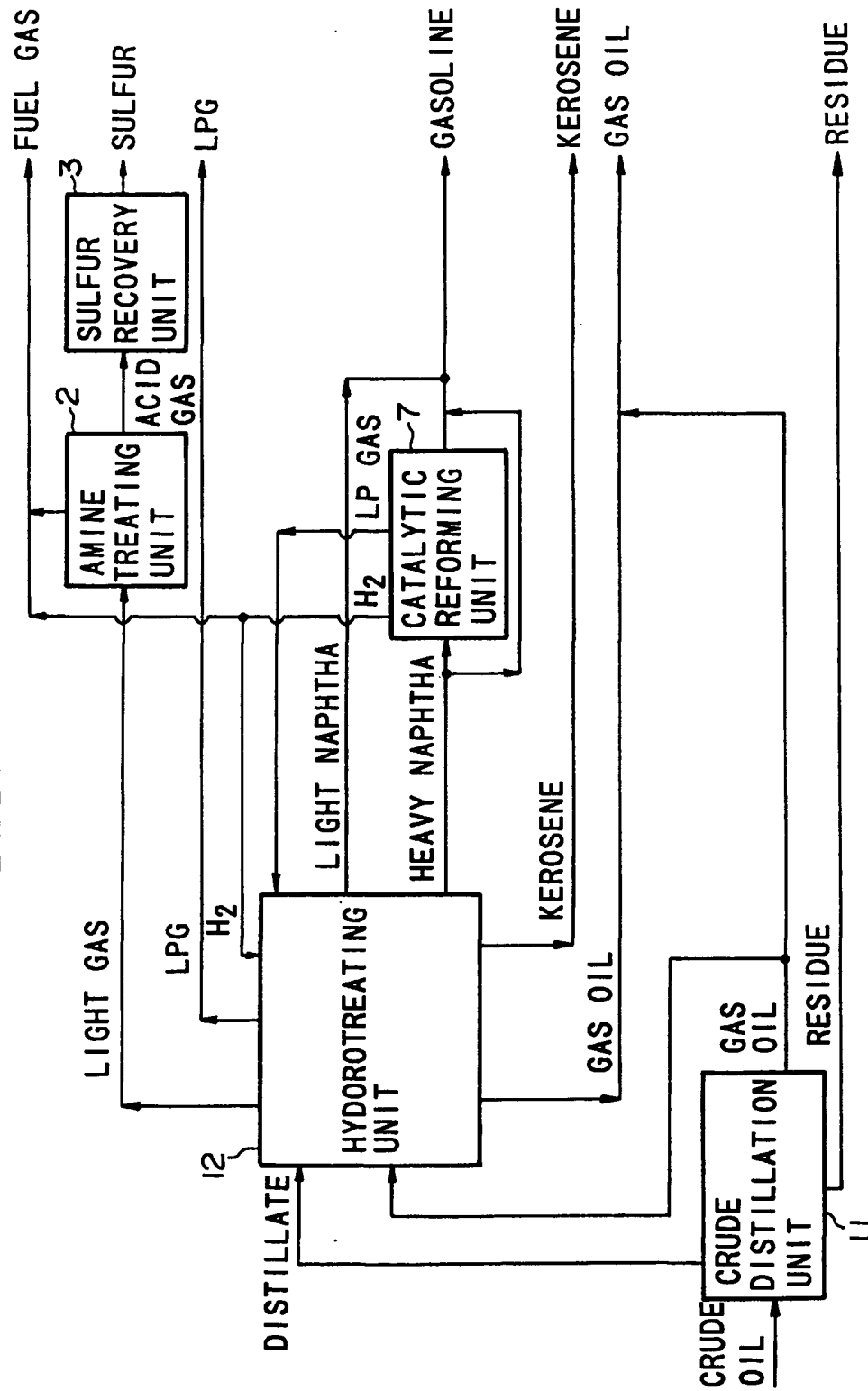


FIG.2

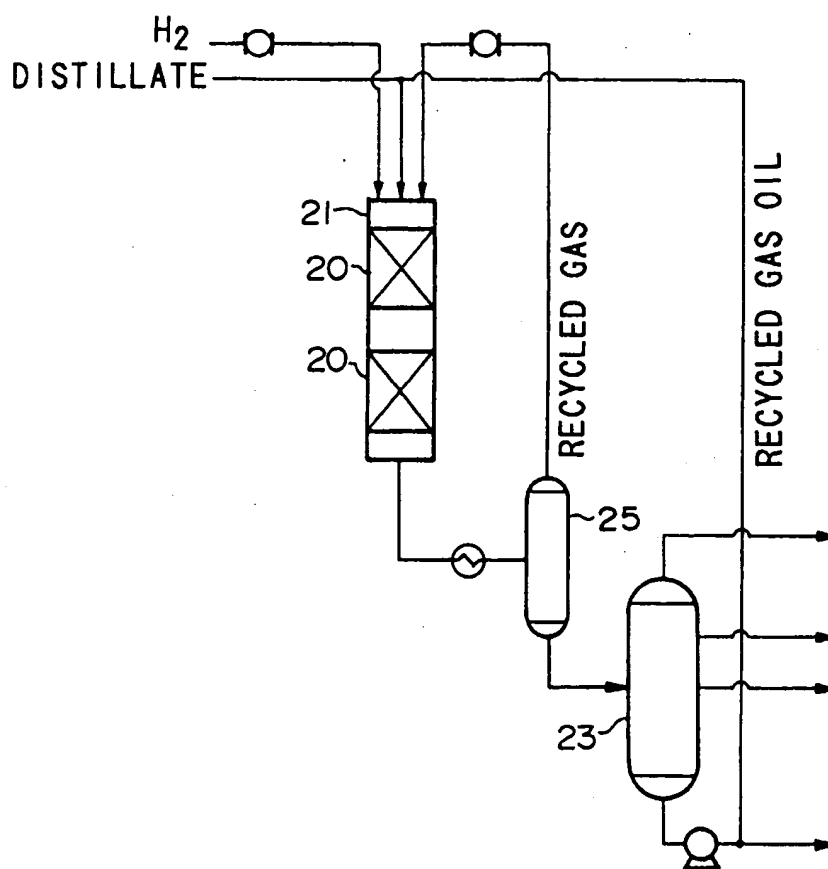


FIG.3

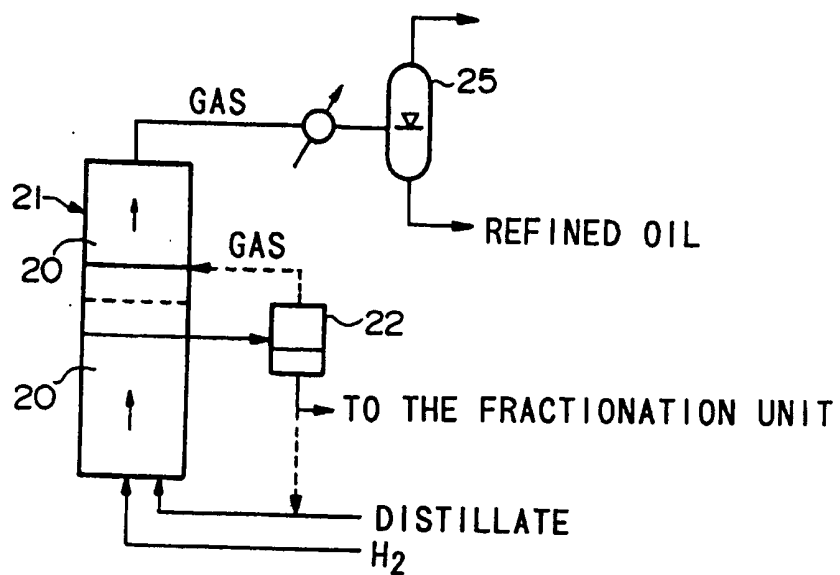


FIG.4

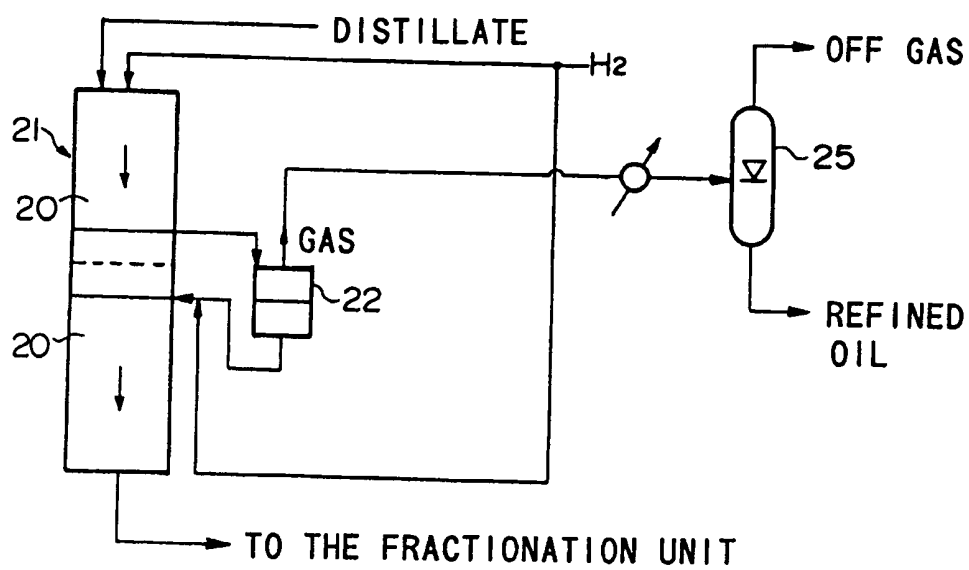


FIG.5

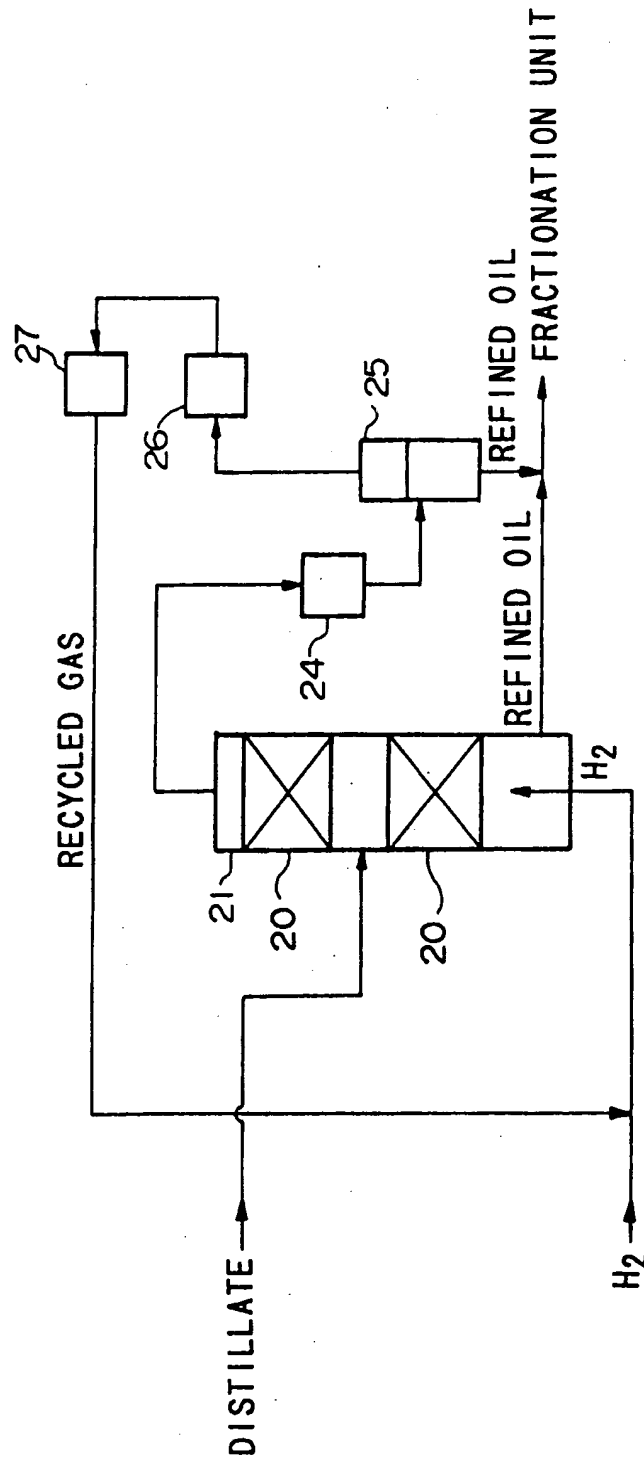


FIG.6

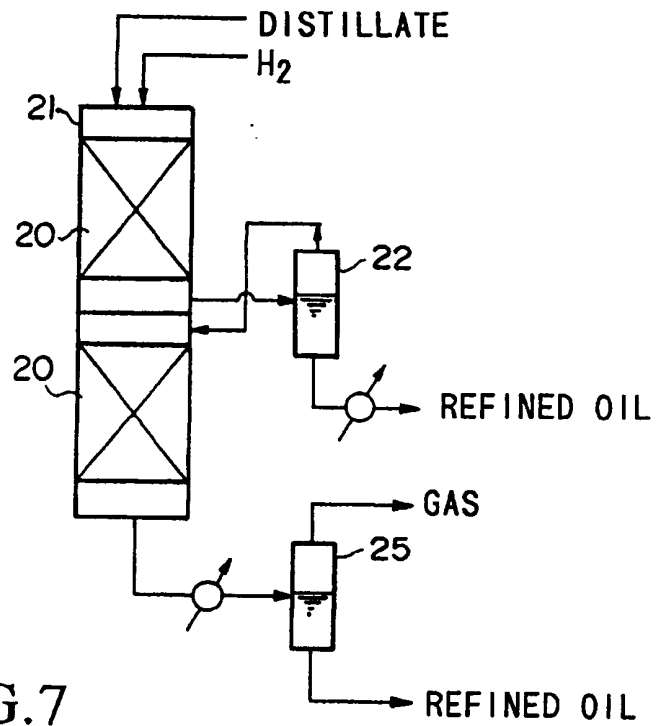


FIG.7

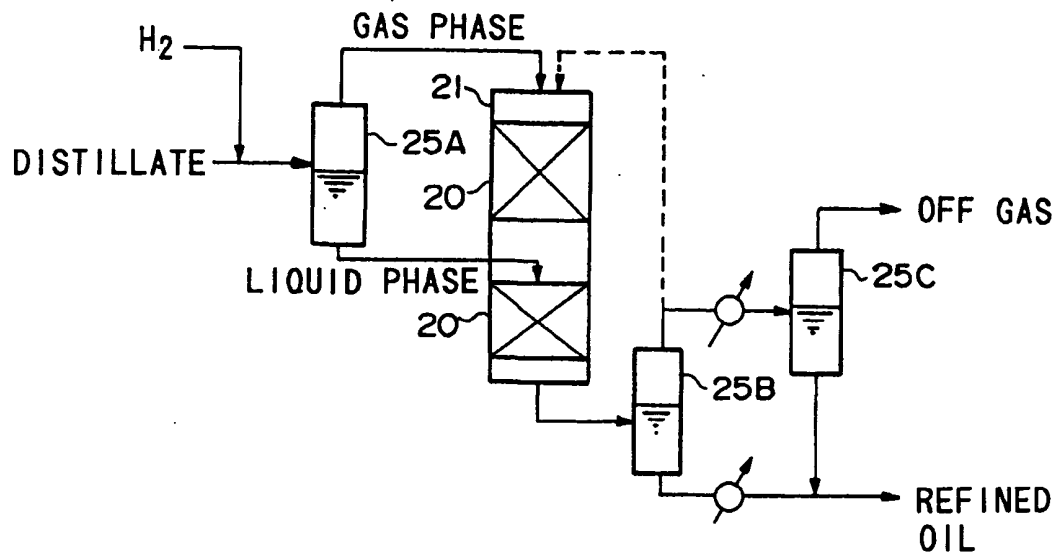
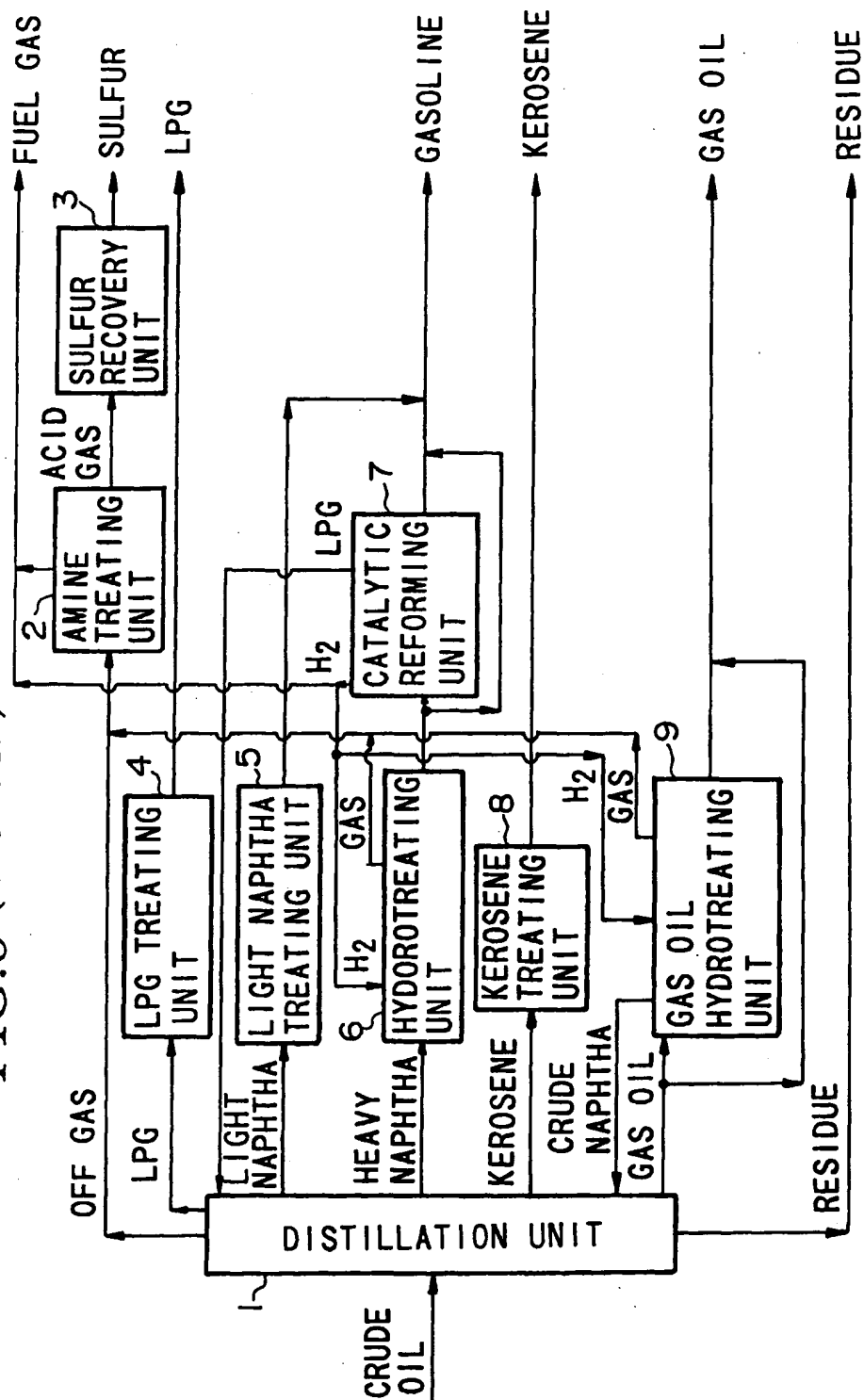




FIG. 8 (PRIOR ART)





⑫ **EUROPEAN PATENT APPLICATION**

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⑦① Applicant : **JGC CORPORATION**  
**2-1, Otomachi 2-chome**  
**Chiyoda-ku**  
**Tokyo (JP)**

⑦② Inventor : **Kondo, Sadao, c/o Yokohama Office,**  
**JGC Corp.**  
**14-1, Bessho 1-chome,**  
**Minami-ku**  
**Yokohama-shi, Kanagawa-ken (JP)**

Inventor : **Tashiro, Natsuo, c/o Yokohama**  
**Office, JGC Corp.**  
**14-1, Bessho 1-chome,**  
**Minami-ku**

**Yokohama-shi, Kanagawa-ken (JP)**  
Inventor : **Ogawa, Akinori, c/o Yokohama**  
**Office, JGC Corp.**

**14-1, Bessho 1-chome,**  
**Minami-ku**

**Yokohama-shi, Kanagawa-ken (JP)**  
Inventor : **Tsuchiya, Fujio, c/o Yokohama**  
**Office, JGC Corp.**

**14-1, Bessho 1-chome,**  
**Minami-ku**

**Yokohama-shi, Kanagawa-ken (JP)**  
Inventor : **Inomata, Makoto, c/o Yokohama**  
**Office, JGC Corp.**

**14-1, Bessho 1-chome,**  
**Minami-ku**

**Yokohama-shi, Kanagawa-ken (JP)**

⑦④ Representative : **Polus, Camille et al**  
**c/o Cabinet Lavoix**  
**2, Place d'Estienne d'Orves**  
**F-75441 Paris Cedex 09 (FR)**

⑤④ **Refining method and its configuration.**

⑤⑦ The present invention relates to a refinery for hydrotreating of petroleum fractions, and more particularly, a refining method and a refinery configuration comprising a step for distillation of a crude oil to separate a residue and a distillate and a step for hydrotreating the distillate at once in a single hydrotreating unit. If compared to the conventional wherein crude oil is distilled into several fractions and hydrotreating is carried out on each fraction independently, the present invention can simplify a refinery configuration and achieves compact plant with low capital investment cost, even for a small scale refinery.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 94 40 1673

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-3 193 495 (ESSO)	1-3, 5, 8-10, 15-17, 19	C10G45/02 C10G69/08
Y	* the whole document *	4, 6, 7, 11-14, 18, 20, 21	
X	US-A-3 050 458 (SHELL OIL) * the whole document *	1-3, 5, 8-10	
Y	US-A-3 801 495 (CHEVRON) * figure 1 *	4, 18	
Y	WO-A-92 08772 (DAVY MCKEE) * claim 1; figure 1 *	6, 11, 20	
Y	US-A-3 268 438 (CHEVRON) * figure 4 *	7, 12-14, 21	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C10G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 June 1995	Examiner Michiels, P
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : technological background O : non-written disclosure P : intermediate document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category		& : member of the same patent family, corresponding document	

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